# PATENT COOPERATION TREATY

# PCT



## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| Applicant's or agent's file reference<br>PE-0641 | **FOR FURTHER ACTION** | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
|---|---|---|
| International application No.<br>PCT/BR 02/00086 | International filing date *(day/month/year)*<br>19.06.2002 | Priority date *(day/month/year)*<br>19.06.2002 |
| International Patent Classification (IPC) or both national classification and IPC<br>C08F10/00 | | |
| Applicant<br>BRASKEM S.A. | | |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 10 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 14 sheets.

3. This report contains indications relating to the following items:

   | | | |
   |---|---|---|
   | I | ☒ | Basis of the opinion |
   | II | ☐ | Priority |
   | III | ☒ | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability |
   | IV | ☒ | Lack of unity of invention |
   | V | ☒ | Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
   | VI | ☐ | Certain documents cited |
   | VII | ☐ | Certain defects in the international application |
   | VIII | ☐ | Certain observations on the international application |

| Date of submission of the demand | Date of completion of this report |
|---|---|
| 02.01.2004 | 15.10.2004 |
| Name and mailing address of the international preliminary examining authority:<br>European Patent Office - P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040 Tx: 31 651 epo nl<br>Fax: +31 70 340 - 3016 | Authorized Officer<br>Parry, J<br>Telephone No. +31 70 340-1032 |

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/BR 02/00086

## I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

**Description, Pages**

| | |
|---|---|
| 2, 3, 5, 6, 8, 9, 11-15, 17-31 | as originally filed |
| 1, 4, 7, 10, 16 | filed with telefax on 30.08.2004 |

**Claims, Numbers**

| | |
|---|---|
| 1-65 | filed with telefax on 30.08.2004 |

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   *(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

   **see separate sheet**

6. Additional observations, if necessary:

**see separate sheet**

## III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☒ claims Nos. 1-65 (in part)

because:

☒ the said international application, or the said claims Nos. 1-65 (in part) relate to the following subject matter which does not require an international preliminary examination (specify):

**see separate sheet**

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/ or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the Standard.

☐ the computer readable form has not been furnished or does not comply with the Standard.

## IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees, the applicant has:

☒ restricted the claims.

☐ paid additional fees.

☐ paid additional fees under protest.

☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

☒ complied with.

☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

   ☐ all parts.

   ☒ the parts relating to claims Nos. 1-65 (in part) .

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

| | | | |
|---|---|---|---|
| Novelty (N) | Yes: | Claims | 1-43,45,59-65 (in part). |
| | No: | Claims | 44,46-58 (in part). |
| Inventive step (IS) | Yes: | Claims | |
| | No: | Claims | 1-65 (in part). |
| Industrial applicability (IA) | Yes: | Claims | 1-65 (in part). |
| | No: | Claims | |

2. Citations and explanations

   **see separate sheet**

**Re Item I**

Basis of the opinion

The following find no support in the application as originally filed and are therefore not allowable (Art. 34 PCT). This report has therefore been established as if these amendments had not been made (R. 70.2(c)):

1. Claim 1: (e) "reducing agent which acts on the titanium centre compound".

2. Claim 1: (f) "capable of acting on the alkoxide compounds"

3. Claims 3, 4 and 34: "diameter" -this cannot be regarded as a correction of an obvious error (or a clarification) as "diameter" is not unambiguously derivable from the orginal term "size".

4. Claim 13: "n varies from 1 to 35".

5. Claim 37: "ranging from 0.01-0.02 g".

6. Claim 38: "ranging from 0.015-0.02 g".

7. Claim 38: "ranging from 0.015-0.02 g".

8. Claim 54: "properties" -this cannot be regarded as a correction of an obvious error as "properties" is not synonymous or unambiguously derivable from the orginal term "structure".

9. Claim 56: "0.38 g/cm3".

10. Claim 58: "fines...per weight" -although the values mentioned in this claim are disclosed in some of the present examples, these specific examples cannot form the basis for a generalisation into the claims.

11. Amended description pages 1,4,7 (both "diameter" and "40-70 um"), 10, and p.16.

**Re Item III**

**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

The Applicant paid for all search fees but has requested in response to form PCT/IPEA/405 that only invention group 4 be examined, thus:

The subject matter of claims 1-65, insofar as it relates to step (a) of claim 1 where a group 13 organometallic compound is employed.

**Re Item IV**

**Lack of unity of invention**

As the result of the restriction as outlined in Box III above, there is no lack of unity in the present application.

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. The following documents (D1, D3-D4) will be referred to:

D1: EP-A-0522651
D3: EP-A-0045885
D4: EP-A-0480435

2. D1 describes a microspheroidal silica support with the following characteristics: SA = 320 m2/g, pore volume= 1.6 ml/g, av. pore diameter= 25 A, particle size =40 microns. Eg 1 describes the following preparation of a catalyst composition therewith, the brackets delimiting individual stages: (17 g silica + effectively a solution of an equilibrium mixture comprising Mg(octyl)2 and Mg(ethyl)2 and their corresponding "mixed magnesium alkyl" species, followed by solvent removal) + ( ethylacetate + 4.96 g TiOBu4 (supplying the "alkoxy groups) + TiCl4 + 2.79 g MgCl2) + 35.6 mmol EtAlCl2 chlorinating agent), the whole heated to 66 °C for 1 hour and then washed with hexane to yield the following composition in the final product (wt.% vs total composition weight): 4.3% Ti, 2.2% Al, 18.4 % Cl 3.8% Mg. This is subsequently employed in ethylene polymerisation in an autoclave under pressure in conjunction with 50 mole equivalents of Et3Al per Ti atom. Eg 4 (comparative) discloses a similar preparation in which no additional TiCl4 is added (see p.4, l.1- p.6, l.40 and claim 11). **No evidence has been provided which shows that the polymers produced according to D1 differ from those of the present application, for example, with respect to bulk density and fines, hence claims 44,46-58 are not novel.**

3. The subjective problem to be solved is to provide polymers with improved properties by employing catalysts produced by a process which leads to them not being excessively active at the start-up of polymerisation. Present claim 1 differs in that the organometallic group 13 compound, which in D1 is also the chlorinating agent, is impregnated into the support separately in step (a) (feature 1), the ratio of the amount of silica support to catalyst component used (feature 2), the ratio of the amount of silica support hydroxyl groups to organometallic component(s) used and the nature of said components (feature 3), the ratio of the amount of silica to magnesium component used (feature 4). The technical effect of these features have not been demonstrated over D1. Thus the problem to be solved can only be regarded as to provide alternative processes for producing solid ethylene polymerisation catalysts. It is trivial starting from D1, considered the closest prior art as described in point 2 above, to add EtAlCl2 to the support separately and obvious in any case to reduce the amounts of catalytic reagents used with respect to the silica support (ie effectively to dilute the catalyst), if a lower start-up polymerisation activity is desired. **Hence claims 1-14,19,22,24-26,31-34,40, and 42 are not considered inventive.**

4. It is trivial to select other halogen-bearing compounds which are standard in the art as halogenating agents. **Hence claims 20-21 are not inventive.**

5. In the absence of any demonstrated technical effect, it is trivial to prolong the thermal treatment. **Hence claim 23 is not inventive.**

6. D1 is silent with respect to the method by which the catalyst is fed into the reactor but whatever the method used, it must necessarily be one of those disclosed in present **claim 49, hence this claim is also not inventive.**

7. D1, which is considered to be the closest prior art, describes the above-mentioned catalytic system. The subject-matter of claims 15-18 further differs in that a reducing agent is present (feature 5). The technical effect of this reducing agent has not been demonstrated. Therefore the objective problem can only be formulated as to provide alternative catalyst compositions for olefin polymerisation catalysts. The solution proposed in claims 15-18 of the present application cannot be considered as involving an inventive step because feature 2 is disclosed as such a reductant in D3 where the following preparation is described: (16.6 g of Ti(O-n-C4H9)4+ 2.15 g MGCl2) + 12.5 g SiCl4 + 8.9 g PMHS (p.9, l.9-p.10, eg 1; p.14, eg A; p. 17, table II). The skilled person would therefore regard it as a normal option to combine the teachings of D3 with those of D1 in order to solve the problem of the present application. **Hence claims 15-18 are**

**not inventive.**

8. It is trivial to wash the composition with additional organometallic compounds, together or in varying sequences, a step in the overall process for which no technical effect has been demonstrated. **Hence claims 27-30 are not inventive.**

9. The SA of the silica of 320 m2/g disclosed in D1 differs only marginally from the 300 m2/g mentioned in present **claim 35, hence this claim is not considered inventive.**

10. The pore volume of the silica of 1.6 ml/g disclosed in D1 differs only marginally from the 1.0 ml/g mentioned in present **claim 36, hence this claim is not considered inventive.**

11. The parameter relative weights of magnesium titanium and organometallic compound are only slightly lower than the corresponding values disclosed in D1. **Hence claims 37-39 respectively are not considered inventive.**

12. The amount of alkoxy function pertaining to the amount of titanium present in the composition of D1 cannot be calculated. The amount disclosed in **present claim 41** must necessarily range from greater than 0 to less than or equal to 4 times that of the amount of titanium, **hence claim 41 is not considered inventive.**

13. The parameter relative weight of Cl is only slightly lower than the corresponding values disclosed in D1. **Hence claim 43 is not considered inventive.**

14. Gas phase polymerisation using silica-supported catalysts is standard in the art, **hence claim 45 is not inventive.**

15. D1 is silent with respect to the method by which the catalyst is fed into the reactor, but the procedures of **claims 50-52** are entirely standard in the art, **hence these claims are not inventive.**

16. It is trivial to apply the teachings of the examples of D1 to copolymerisation processes (which are in any case mentioned in the description of D1). **Hence claims 59-65 are not inventive.**

17. D4 describes the following preparation: microspheroidal silica, SA = 320 m2/g, pore volume 1.65ml/g, av. pore diameter: 25 nm, av. particle size: 40 microns), which is

employed in Eg 1 as follows: (11.4 g silica + effectively a mixture of MgOct2+ MgEt2) + (ethylacetate + 6.60 g TiOBu4 + 1.87 g MgCl2) + 23.6 mmol EAlCl2 (the chlorinating agent), the whole stirred at 25°C for 15 min followed by washing with hexane. Polyethylene of d = 0.961 is produced therewith in the presence of Et3Al cocatalyst (see p.4, l.1- p.6, l.30). **No evidence has been provided which shows that the polymers produced according to D4 differ from those of the present application, for example, with respect to bulk density and fines, hence claims 44,46-58 are not novel.**

**Re Item VII**
**Certain defects in the international application**
1. No distinction has been made between examples of the present invention and any examples not according to the present invention which may serve as comparisons.

**Re Item VIII**
**Certain observations on the international application**
The following objections are made under Art. 6 (PCT):
1. Claim 1, step 1 (e): it is not clear what compound (presumably it is the titanium centre) is being acted on by the reducing agent. That is, the "reducing agent" is ill-defined.

2. Claim 1, step 1 (f): it is not clear what compound is being acted on by the halogenating agent. That is, the "halogenating agent" is ill-defined.

3. Claim 3 : "size" is unclear: which dimension is being measured?

4. Claim 7: only compounds of group 2 and 13 metals are recited in this claim.

5. Claim 12,24: the term "usual methods" is unclear.

6. Claim 16 "n" has not been defined.

7. Claim 19: Ethylaluminium dichloride represents the empirical formula of ethylaluminium sesquichloride, so the former is redundant.

8. Claim 32: (i) it cannot be ascertained that the catalyst component product had been prepared beforehand in this way (ii) "...high activity and low decay..." describes a result to be achieved.

9. Claim 34: "size" is unclear: which dimension is being measured?

10. Claims 53-65 are "product by process" claims. Furthermore it is not evident, even if the nature of the comonomer and its incorporation is varied, how such varied polymers ranging from low to high density could be produced by the same process. Moreover the terms "low xylene...", "small quantity of fines", and "narrow molecular weight" are meaningless as the density has not been defined with respect to a point of reference. The terms in claims 54,55 and 57 concerning "bulk density" and "fines" effectively amount to results to be achieved.